

PATENT ABSTRACTS OF JAPAN

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C09J179/00

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(71)Applicant : TOYO INK MFG CO LTD

(22)Date of filing : 22.09.1997

(72)Inventor : YAMAGUCHI TAKEO

(54) CURABLE RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a resin composition which can be cured by merely letting it standing at a room temperature and has excellent storage stability by mixing a resin obtained by the Michael addition reaction of a specified (meth)acryl- containing compound with an aminic active hydrogen containing compound with a resin having non-aminic active hydrogen atoms and epoxy-containing compound.

SOLUTION: This composition comprises a resin (A) having a weight-average molecular weight of 1,000-1,000,000 and prepared by the Michael reaction of 20-95 wt. % compound (a) having at least two acrylic or methacrylic groups in the molecule and having a weight-average molecular weight of below 1,000 with 5-80 wt. % compound having at least two aminic active hydrogen atoms in the molecule, a resin (B1) having non-aminic active hydrogen atoms and an epoxy-containing compound (C). B1 and C may be replaced by a resin (B2) having non-aminic active hydrogen atoms and epoxy groups. The non-aminic active hydrogen atom is exemplified by a hydroxylic or carboxylic one.

LEGAL STATUS

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N 1999:225729 CAPLUS
 DN 130:313249
 ED Entered STN: 12 Apr 1999
 TI Storage-stable, room-temperature-curable coating compositions
 IN Yamaguchi, Takeo
 PA Toyo Ink Mfg. Co., Ltd., Japan
 SO Jpn. Kokai Tokkyo Koho, 7 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 IC ICM C08G059-40
 ICS C08G073-02; C08L063-00; C08L079-00; C09D163-00; C09D179-00;
 C09J163-00; C09J179-00
 CC 42-7 (Coatings, Inks, and Related Products)
 Section cross-reference(s): 37

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PRAI	JP 1997-256291		19970922		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 11092546	ICM	C08G059-40
	ICS	C08G073-02; C08L063-00; C08L079-00; C09D163-00; C09D179-00; C09J163-00; C09J179-00

AB The title comps. contain (A) resins (Mw 1000-1,000,000) obtained by Michael addition reaction of 20-95% comps. (Mw <1000) having ≥2 (meth)acrylic groups with 5-80% comps. having ≥2 active H atoms of amines, (B1) resins having active H atoms other than amines, and (C) epoxy-containing comps. Alternatively, the comps. contain the resins (A) as above and (B2) resins having both epoxy groups and active H atoms other than amines. Thus, Michael addition reaction of BuNH2 3.65, 2,2-dimethylpropane-1,3-diol diacrylate 5.31, and trimethylolpropane triacrylate 7.41 g in MeOH gave a solution containing a polymer (Mw 30 + 103), which was stirred with an EtOAc solution of 2-acetoacetoxyethyl methacrylate-Me methacrylate copolymer and Ph glycidyl ether to give a solution showing good stability for 1 wk. The

solution was cast on a glass plate and dried to give a film showing residues after EtOAc extraction 90%.

ST acrylate amine **Michael** addn epoxy coating; methacrylate amine **Michael** addn epoxy coating storage stability

IT Amines, reactions

RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction products, adducts with (meth)acrylates, copolymers;
 storage-stable room-temperature-curable resin coating comps. containing

epoxy comps. and **Michael** addition products of amines with (meth)acrylates)

IT Coating materials
 (room-temperature-curable; storage-stable room-temperature-curable resin
 coating comps. containing epoxy comps. and **Michael** addition products of amines with (meth)acrylates)

IT **Michael** reaction
 (storage-stable room-temperature-curable resin coating comps. containing epoxy

comps. and **Michael** addition products of amines with (meth)acrylates)

IT 80-62-6DP, polymers with acrylic-amine adducts, acrylates, and epoxy
 comps. 97-88-1DP, polymers with acrylic-amine adducts, acrylates, and
 epoxy comps. 100-42-5DP, polymers with acrylic-amine adducts,

acrylates, and epoxy compds. 106-91-2DP, polymers with acrylic-amine adducts, acrylates, and epoxy compds. 109-73-9DP, 1-Butanamine, **Michael** adducts with acrylates, polymers with acrylates and epoxy compds., uses 111-26-2DP, 1-Hexanamine, **Michael** adducts with acrylates, polymers with acrylates and epoxy compds. 111-86-4DP, 1-Octanamine, **Michael** adducts with acrylates, polymers with acrylates and epoxy compds. 122-60-1DP, polymers with acrylic-amine adducts, acrylates, and epoxy compds. 868-77-9DP, polymers with acrylic-amine adducts, acrylates, and epoxy compds. 2223-82-7DP, **Michael** adducts with amines, polymers with acrylates and epoxy compds. 3524-68-3DP, **Michael** adducts with amines, polymers with acrylates and epoxy compds. 4986-89-4DP, **Michael** adducts with amines, polymers with acrylates and epoxy compds. 15625-89-5DP, **Michael** adducts with amines, polymers with acrylates and epoxy compds. 21282-97-3DP, polymers with acrylic-amine adducts, acrylates, and epoxy compds. 26570-48-9DP, **Michael** adducts with amines, polymers with acrylates and epoxy compds. 61722-28-9DP, **Michael** adducts with amines, polymers with acrylates and epoxy compds. 91433-85-1DP, **Michael** adducts with amines, polymers with acrylates and epoxy compds.
RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)

(storage-stable room-temperature-curable resin coating compns. containing epoxy compds. and **Michael** addition products of amines with (meth)acrylates)

DERWENT-ACC-NO: 1999-283606

DERWENT-WEEK: 199927

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TITLE: Curable resin composition - includes resin which is prepared by Michael addition reaction of compound which has at least two (meth)acrylic groups per molecule with compound having at least two amino active hydrogens

PATENT-ASSIGNEE: TOYO INK MFG CO LTD[TOXW]

PRIORITY-DATA: 1997JP-0256291 (September 22, 1997)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 11092546 A	April 6, 1999	N/A	007	C08G 059/40

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP 11092546A	N/A	1997JP-0256291	September 22, 1997

INT-CL (IPC): C08G059/40, C08G073/02, C08L063/00, C08L079/00, C09D163/00, C09D179/00, C09J163/00, C09J179/00

ABSTRACTED-PUB-NO: JP 11092546A

BASIC-ABSTRACT:

A curable resin compsn. comprises: (A) a resin having a wt. average molecular wt. (Mw) of 1000-1,000,000; (B1) a resin having active hydrogens other than amino active hydrogens; and (C) an epoxy gp.-contg. cpd.

(A) is prepared by Michael addition reaction of: (a) 20-95 wt. % of a cpd. which has at least two (meth)acrylic gps. per molecule and has a Mw of less than 1000; with (b) 5-80 wt.% of a cpd. having at least two amino active hydrogens.

Also claimed is a curable resin compsn. consisting of: (A) as above; and (B2) a cpd. which has active hydrogens other than amino active hydrogens and an epoxy gp.

USE - The resin compsn. is useful for coatings, adhesives, pressure-sensitive adhesives, inks, fillers and moulding materials.

ADVANTAGE - The resin compsn. has good storage stability and is curable at room temp.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: CURE RESIN COMPOSITION RESIN PREPARATION MICHAEL ADD REACT
COMPOUND TWO METHO ACRYLIC GROUP PER MOLECULAR COMPOUND TWO AMINO
ACTIVE

DERWENT-CLASS: A21 A81 A82 G02 G03

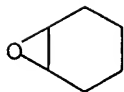
CPI-CODES: A07-A04; A08-C01; A08-D01; G02-A02; G02-A02B2; G02-A04A; G03-B02;
G03-B02E;

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]

018 ; H0022 H0011 ; G0873*R G0817 D01 D51 D54 D57 D63 D26 D11 D10
G0975*R D55 D58 ; G1672*R G1649 D01 F09 F07 G1809*R F10 ; H0022

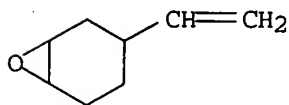
RN 286-20-4 REGISTRY
 ED Entered STN: 16 Nov 1984
 CN 7-Oxabicyclo[4.1.0]heptane (8CI, 9CI) (CA INDEX NAME)
 OTHER NAMES:
 CN **1,2-Cyclohexene oxide**
 CN 1,2-Epoxy cyclohexane
 CN 2,3-Tetramethyleneoxirane
 CN cis-1,2-Epoxy cyclohexane
 CN cis-7-Oxabicyclo[4.1.0]heptane
 CN **cis-Cyclohexene oxide**
 CN Cyclohexane, 1,2-epoxy-
 CN Cyclohexene epoxide
 CN **Cyclohexene, oxide**
 CN Cyclohexylene oxide
 CN NSC 128074
 CN NSC 5218
 CN Tetramethyleneoxirane
 FS 3D CONCORD
 DR 137422-07-2, 26637-95-6, 28165-18-6
 MF C6 H10 O
 CI COM, RPS
 LC STN Files: AGRICOLA, ANABSTR, BEILSTEIN*, BIOBUSINESS, BIOSIS,
 BIOTECHNO, CA, CANCERLIT, CAOLD, CAPLUS, CASREACT, CHEMCATS,
 CHEMINFORMRX, CHEMLIST, CHEMSAFE, CSCHM, CSNB, DETHERM*, EMBASE,
 ENCOMPLIT, ENCOMPLIT2, ENCOMPPAT, ENCOMPPAT2, GMELIN*, HODOC*, HSDB*,
 IFICDB, IFIPAT, IFIUDB, MEDLINE, NIOSHTIC, PS, RTECS*, SPECINFO,
 SYNTHLINE, TOXCENTER, USPAT2, USPATFULL
 (*File contains numerically searchable property data)
 Other Sources: DSL**, EINECS**, TSCA**
 (**Enter CHEMLIST File for up-to-date regulatory information)



****PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT****

3985 REFERENCES IN FILE CA (1907 TO DATE)
 127 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
 3992 REFERENCES IN FILE CAPLUS (1907 TO DATE)
 40 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

RN 106-86-5 REGISTRY
 ED Entered STN: 16 Nov 1984
 CN 7-Oxabicyclo[4.1.0]heptane, 3-ethenyl- (9CI) (CA INDEX NAME)
 OTHER CA INDEX NAMES:
 CN 7-Oxabicyclo[4.1.0]heptane, 3-vinyl- (6CI, 8CI)
 CN Cyclohexane, 1,2-epoxy-4-vinyl- (7CI)
 OTHER NAMES:
 CN 1,2-Epoxy-4-vinylcyclohexane
 CN **1-Ethenyl-3-cyclohexene oxide**
 CN 1-Vinyl-3,4-epoxycyclohexane
 CN 3,4-Epoxycyclohexylethylene
 CN 3-Ethenyl-7-oxabicyclo[4.1.0]heptane
 CN 3-Vinyl-7-oxabicyclo[4.1.0]heptane
 CN 4-Vinyl-1-cyclohexene-1,2-epoxide
 CN 4-Vinylcyclohexane 1,2-epoxide
 CN 4-Vinylcyclohexane-1-oxide
 CN 4-Vinylcyclohexene monoepoxide
 CN **4-Vinylcyclohexene oxide**
 CN Epoxide 101
 CN NSC 35409
 CN Unoxat epoxide 101
 CN Vinyl-3,4-epoxycyclohexane
 FS 3D CONCORD
 DR 29087-40-9
 MF C8 H12 O
 CI COM
 LC STN Files: BEILSTEIN*, BIOSIS, CA, CAOLD, CAPLUS, CASREACT, CHEMCATS,
 CHEMINFORMRX, CHEMLIST, CIN, CSCHM, EMBASE, IFICDB, IFIPAT, IFIUDB,
 NIOSHTIC, RTECS*, TOXCENTER, USPAT2, USPATFULL
 (*File contains numerically searchable property data)
 Other Sources: DSL**, EINECS**, TSCA**
 (**Enter CHEMLIST File for up-to-date regulatory information)



****PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT****

395 REFERENCES IN FILE CA (1907 TO DATE)
 141 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
 395 REFERENCES IN FILE CAPLUS (1907 TO DATE)
 19 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the resin constituent with which it is used a coating, adhesives, a binder, ink, a bulking agent, and for molding materials and which is hardened at a room temperature after pouring in into spreading or a mold.

[0002]

[Description of the Prior Art] The hardenability resin constituent using active hydrogen, such as a carbonyl group, represented by the acetoacetoxy group is illustrated by a USP No. 4,408,018 official report, JP,1-121341,A, JP,1-204919,A, a USP No. 5,017,649 official report, JP,6-167355,A, JP,7-173262,A, etc. Although these had the description in the curing catalyst, all had the trouble that a curing catalyst did not show hardening sufficient at a room temperature which is not mixed with resin and mutual, or preservation for one week or more could not be performed in the state of the coating liquid before spreading, respectively.

[0003]

[Problem(s) to be Solved by the Invention] Artificers found out that the mixture of the resin obtained by the reaction of an epoxy compound and amine nature active hydrogen, and an acrylic (meta) radical promoted the reaction of active hydrogen and an acrylic (meta) radical remarkably. And this is used, and it is only left at a room temperature, and can harden, and the resin constituent excellent in preservation stability is offered.

[0004]

[Means for Solving the Problem] This invention has an acrylic radical or two or more methacrylic radicals in 1 molecule. weight average molecular weight -- less than 1000 (Compound a) 20-95 % of the weight -- and The weight average molecular weight to which it comes to carry out the Michael addition reaction of the (Compound b) 5-80 % of the weight which has two or more active hydrogen of amino nature in 1 molecule The resin of 1,000-1,000,000 (A), It is related with the hardenability resin constituent which consists of resin (B1) which has active hydrogen other than the amino group, and a compound (C) which has an epoxy group. Moreover, it is related with the hardenability resin constituent with which the weight average molecular weight to which it comes to carry out the Michael addition reaction of the (Compound b) 5-80 % of the weight to which it has an acrylic radical or two or more methacrylic radicals in 1 molecule, and weight average molecular weight has two or more active hydrogen of amino nature in less than 1000 (Compound a) 20-95 % of the weight and 1 molecule consists of resin (B-2) which has the active hydrogen and the epoxy groups other than the resin (A) of 1,000-1,000,000, and the amino group. Moreover, active hydrogen other than the amino group is related with the above-mentioned hardenability resin constituent characterized by being the methine hydrogen or methylene hydrogen permuted by two pieces or three functional groups which are independently chosen from a carbonyl group, a carboxyl group, a carbamoyl group, a cyano group, or a nitro group. Furthermore, it is related with the above-mentioned hardenability resin constituent characterized by including a compound (a) one to 80% of the weight to the whole resin constituent.

[0005]

[Embodiment of the Invention] Into 1 molecule used by this invention, it has an acrylic radical or two or more methacrylic radicals, and the Pori (meta) acrylic ester of polyfunctional alcohol or a polyfunctional phenol is mentioned for weight average molecular weight as less than 1000 compound (a), for example.

[0006] Specifically, it is the di(meth)acrylate of 2 organic-functions alcohol, such as ethylene glycol, propylene glycol, diethylene-glycol, dipropylene glycol, triethylene glycol, tripropylene glycol, tetraethylene glycol, tetrapropylene glycol, polyethylene-glycol, polypropylene-glycol, butanediol, 2, and 2-dimethyl propanediol, pentanediol, and hexandiol, and [0007]. A phthalic acid, hexahydrophthalic acid, a maleic acid, a succinic acid, a malonic acid, The di(meth)acrylate of the polyalkylene glycol denaturation object of 2 organic-functions carboxylic acids, such as hexanedioic acid, or an epichlorohydrin denaturation object, The Pori (meta) acrylate of the polyalkylene glycol denaturation object of the carboxylic acid more than trivalent [of trimellitic acid, pyromellitic acid, hexahydro pyromellitic acid, etc.], or an epichlorohydrin denaturation object, The di(meth)acrylate of the epichlorohydrin denaturation object of the bisphenol A derivative, the Pori (meta) acrylate of the polyalkylene glycol denaturation object of an iso SHINURU acid derivative, [0008] The Pori (meta) acrylate of polyfunctional phenols, such as the Pori (meta) bitter taste lied of polyfunctional alcohol, such as a glycerol, trimethylol propane, pentaerythritol, dipentaerythritol, a mannitol, and a sorbitol, the polyalkylene glycol denaturation object of those, or an epichlorohydrin denaturation object, a catechol, resorcinol, a hydroquinone, a FURORO glycine, and pyrogallol, etc. is mentioned. Two or more sorts of these may be used.

[0009] moreover, as a compound (b) which is used by this invention and which has two or more active hydrogen of amino nature in 1 molecule Monomethylamine besides ammonia, ethylamine, propylamine, A butylamine, pentylamine, hexylamine, cyclohexylamine, A heptyl amine, an octyl amine, methylhydrazine, an ethyl hydrazine, Alkylene chains, such as benzylamine, phenethylamine, N, and N-dimethyl propylamine, And the amine, methoxyethoxy ethoxy ethylamine which have the one 1st class amino group, Polyalkylene chains, such as methoxy propyl propylamine and methoxy polyethyleneoxy ethylamine, And the amine which has the one 1st class amino group, ethylenediamine, propylenediamine, 1, 6-hexa diamine, diethylenetriamine, triethylenetetramine, The amine which has two or more secondary amine, such as the amine and N which have the two or more 1st class amino groups, such as a melamine, and N'-dimethyl ethylenediamine, Moreover, the amine which has functional groups which have partial saturation double bonds, such as annular amines, such as a piperazine, and allylamine, such as an amine and ethanolamine, is mentioned. Moreover, the compound which has two or more secondary amine which permutes some active hydrogen and is obtained by ethyl acrylate or the methyl chloride in the amine which has the two or more above-mentioned 1st class amines may be used. Two or more sorts of these amines may be used.

[0010] The resin (A) used by this invention has an acrylic radical or two or more methacrylic radicals in 1 molecule, makes the (Compound b) 5-80 % of the weight to which weight average molecular weight has the one or more 1st class amino groups or the two or more 2nd class amino groups in less than 1000 4 (Compound a) 20-95 % of the weight and 1 molecule react, and is obtained. This reaction is a polymerization reaction by carrying out Michael addition between the acrylic (meta) radical of a compound (a), and the amino group of a compound (b). A Michael addition reaction is ordinary pressure, and a compound (a) and a compound (b) are agitated or vibrated, and it makes them react within a container as generally known. Although it is compoundable also in a non-solvent, if the inside of ether system solvents, such as alcoholic solvent, such as amide system solvents, such as N,N-dimethylformamide, N,N-dimethylacetamide, and hexa methyl phospho RASUTORIAMIDO, a methanol, ethanol, propanol, and a butanol, diethylether, dioxane, and a tetrahydrofuran, or solvents, such as water, is used, the reaction rate of resin (A) will improve.

[0011] Although the temperature of reaction time reacts at a room temperature and serves as resin (A) when a compound (a) contains an acrylic radical, you may heat to solvent rotary flow temperature after neglect at a room temperature for the improvement in molecular weight. Reaction time is made to react on the conditions for about three days from 5 minutes. When the obtained resin (A) performs

sedimentation purification by the petroleum ether, a hexane, etc. and a low molecular weight constituent is removed, its physical properties after hardening improve and it is desirable.

[0012] As for the weight average molecular weight of resin (A), it is desirable that it is styrene conversion and is 1,000-1,000,000 in GPC (gel permeation chromatography). It is 3,000-500,000 more preferably. When smaller than this, hardening may become poor by the low molecular weight constituent. Moreover, when larger than this, compatibility with resin (B) worsens. In order to make weight average molecular weight of resin (A) or more into 1000, using together the compound which has three or more acrylic (meta) radicals in 1 molecule as a compound (a), or the compound which has three or more active hydrogen of amino nature in 1 molecule as a compound (b) is recommended.

[0013] In case resin (A) is compounded, theoretically, the loadings ratio of a compound (a) and a compound (b) should have a desirable thing with equal chemical equivalent of the acrylic (meta) radical of a compound (a) and chemical equivalent of the active hydrogen of the amino nature of a compound (b). However, actually, it has the influence of the viscosity of reaction mixture etc., and the ratio of the chemical equivalent is not necessarily related to hardenability. Therefore, in order to make weight molecular weight of resin (A) or more into 1000, the optimum value of the combination will be chosen between (Compound a) 20-95 % of the weight and (Compound b) 5-80 % of the weight.

[0014] Next, active hydrogen as indicated to be active hydrogen other than the amino group of the resin (B-2) which has the active hydrogen and the epoxy groups other than the resin (B1) which has active hydrogen other than the amino group used by this invention, and the amino group by the general formula 1 besides a hydroxyl group, a sulfhydryl group, and a carboxyl group is mentioned.

- $X-CH(Y)-Z$ - (general formula 1)

(Here, although X, Y, and Z do not have especially definition, at least one shows the functional group chosen from a carbonyl group, a carboxyl group, a carbamoyl group, a cyano group, or a nitro group.)

[0015] It is desirable especially that active hydrogen is the methine hydrogen permuted by two or more functional groups chosen independently from a carbonyl group, the carboxyl group, the carbamoyl group, the cyano group, or the nitro group or methylene hydrogen. This is the case where at least two of X, Y, and Z have the above-mentioned functional group, in the above-mentioned general formula 1. As such active hydrogen, malonic-acid residue (X, Z= carboxyl group, Y=H), the aceto acetyl group (X= carbonyl group, Y=H, Z= carboxyl group), the aceto carbamoyl group (X= carbonyl group, Y=H, Z= carbamoyl group), cyanoacetic-acid residue (X= cyano group, Y=H, Z= carboxyl), nitro acetic-acid residue (X= nitro group, Y=H, Z= carboxyl group), etc. are mentioned.

[0016] In order for resin (B1) or resin (B-2) to have these active hydrogen, there is a method of carrying out the polymerization of the monomer which has these active hydrogen, and obtaining it. For example, there is the approach of carrying out vinyl polymerization of the acrylic ester which has active hydrogen, such as 2-hydroxyethyl (meta) acrylate, 2-mercapto ethyl (meta) acrylate, an acrylic acid (meta), and acetoacetoxylethyl (meta) acrylate, (meta).

[0017] Moreover, a copolymer with acrylic (meta) monomers, such as vinyl monomers, such as styrene, vinylpyridine, vinyl pyrrolidone, and vinyl acetate, acrylic-acid (meta) alkyl ester, and acrylic-acid (meta) Pori (alkyloxy) ester, is also further used for the acrylic ester which has the above and active hydrogen (meta) suitably.

[0018] In the case of resin (B-2), it is necessary to carry out copolymerization of the monomer which has epoxy groups, such as glycidyl (meta) acrylate, further.

[0019] In addition, the polymerization object of a bisphenol derivative and an epichlorohydrin derivative which has a hydroxyl group per the epoxy resin which has a hydroxyl group, phenoxy resin, and repeat is mentioned to an end as an example of resin (B1). Moreover, resin (B1) and resin (B-2) may be mixed and used.

[0020] As for the weight average molecular weight of resin (B), it is desirable that it is styrene conversion and is 1,000-2,000,000 in GPC (gel permeation chromatography). It is 10,000-1,000,000 more preferably. When smaller than this, hardening may become poor by the low molecular weight constituent. Moreover, when larger than this, compatibility with resin (A) worsens.

[0021] As for the compound (C) which has the epoxy group used by this invention, epichlorohydrin,

phenyl-glycidyl-ether, styrene oxide, cyclohexene-oxide, butene oxide, glycidyl (meta) acrylate, glycidyl cinnamate, allyl compound phenyl ether, vinyl cyclohexene monoepoxide, 1, and 3-butadienemonoepoxide etc. is mentioned. Two or more sorts of these may be used.

[0022] As for a compound (C), it is desirable to use in addition to resin (A), resin (B1), or the whole resin of resin (B-2) by 1 - 100% of the weight of the ratio. Although a compound (C) is not indispensable when resin (B-2) is used, it is used suitably. In this case, it is desirable that the epoxy monomer of resin (B-2) and the sum total of a compound (C) use in addition to the whole resin by 1 - 100% of the weight of the ratio.

[0023] In order to improve the hardenability of the resin constituent of this invention, it is desirable to use said compound (a) in addition to the whole resin by 1 - 80% of the weight of the ratio.

[0024] Resin (A), resin (B1) or resin (B-2), and the need are accepted, and it is made to agitate, rotate or vibrate within a container, mixes, and let a compound (C) or a compound (a) be a resin constituent. At this time, heat 150 degrees C or less may be applied, and uniform mixing may be promoted. Moreover, coloring agents, such as a titanium white and various pigments, lubricant, etc. may be added. When carrying out optical processing, various sensitizing dye may be added further.

[0025] Although the resin constituent of this invention is hardened at a room temperature, it may promote hardening by processing of heat, light, or an electron ray. When heat-treating, it heats below 250 degrees C. Although there is especially no definition in a heat source, generally heat circuit system oven or a heating roller is used. When carrying out optical processing, there is especially no definition in the light source, and a mercury lamp, a xenon lamp, a metal halide lamp, a fluorescent lamp, an incandescent lamp, various laser, etc. are mentioned to it. Moreover, when processing with an electron ray, the inside low voltage electron accelerator of various kinds is used.

[0026]

[Example] Next, although an example explains this invention to a detail further, this invention is not limited to this.

[0027] (Synthetic example 1) Butylamine (BA) 1 evening churning of 3.65g, 2,2-dimethyl propane 1, 3-diol diacrylate (NP) 5.31g, and the trimethylolpropane triacrylate (TMP) 7.41g was carried out at the room temperature in methanol 15.0g, and the resin (A-1) solution was obtained. The weight average molecular weight was shown in a table 2.

(Synthetic examples 2-5) Resin solution (A-1) - (A-10) was obtained using the compound (a) which showed the compound (b) shown in a table 1 in a table 1 instead of the butylamine of the synthetic example 1 instead of 2,2-dimethyl propane 1 of the synthetic example 1, and 3-diol diacrylate. The weight average molecular weight was shown in a table 2. in addition, the inside of a table and HA -- hexylamine, OA octyl amine, and 9EG -- a pentaerythritol thoria chestnut rate and PE4 show pentaerythritol tetraacrylate, and, as for propylene oxide denaturation bisphenol A diacrylate (product made from the Kyoeisha chemistry), and DCP, in DPE, hydrogenation dicyclopentadienyl diacrylate (product made from the Kyoeisha chemistry) and PE3 show [polyethylene-glycol diacrylate (product made from the Kyoeisha chemistry), and BP] dipentaerythritol hexaacrylate.

[0028]

Table 1----- Synthetic example (resin solution) Compound (a) Compound (b)
The inside of () More than g The inside of () More than g ----- 1 (A-1) BA (3.65)
NP (5.31) TMP (7.41) 2 (A-2) BA (3.65) NP (6.37) TMP (5.93) 3 (A-3) BA (3.65) 9EG(s) (13.06) PE3
(7.45) 4 (A-4) HA (5.06) BP (14.22) PE4 (8.81) 5 (A-5) OA (6.46) DCP (7.55) DPE (14.46) -----
----- [0029]

A table 2 ----- A synthetic example (resin solution) Styrene equivalent weight
average molecular weight ----- 1 (A-1) 3.0x103 2 (A-2) 2.5x103 3 (A-3) 2.0x103 4
(A-4) 3.5x103 5 (A-5) 4.0x103 ----- [0030] (Synthetic example 6) Dissolved 2-

acetoacetoxylethylmethacrylate (AAEM) 50g and methyl methacrylate (MMA) 50g and azobisisobutyronitril 3g in 100g of ethyl acetate, it was made to react at rotary flow temperature under nitrogen-gas-atmosphere mind for 8 hours, and the resin solution (B1-1) was obtained.

(Synthetic examples 7-10) Resin solution (B1-2) - (B-2 -2) was obtained instead of the

acetoacetoxylethylmethacrylate of the synthetic example 6, and methyl methacrylate using the monomer shown in a table 3. The weight average molecular weight was shown according to a table 4. Among a table, in 2-cyano acetoxy ethyl methacrylate and BMA, butyl methacrylate and GMA express glycidyl methacrylate and HEMA expresses [ST / styrene and CAEM] 2-hydroxyethyl methacrylate.

[0031]

A table 3 ----- Synthetic example (resin solution) Monomer The inside of () More than g ----- 6 (B1-1) AAEM(50) MMA (50) 7 (B1-2) AAEM(50) ST (50) 8 (B1-3) CAEM (50) BMA (50) 9 (B-2 -1) AAEM(50) MMA(45) GMA(5) 10 (B-2 -2) HEMA(5) MMA (90) GMA (5) ----- [0032]

A table 4 ----- Synthetic example (resin solution) Styrene equivalent weight average molecular weight ----- 6 (B1-1) 4.7×10^4 7 (B1-2) 5.4×10^4 8 (B1-3) 4.6×10^4 9 (B-2 -1) 6.0×10^4 10 (B-2 -2) 6.5×10^4 ----- [0033]

(Example 1) After carrying out cast coating of the 100g [of resin (A-1) solutions], 100g [of resin (B1-1) solutions], and phenyl-glycidyl-ether (PGE) 20g to the glass plate by 50 micrometers in thickness after 3-hour churning mixing at the room temperature and drying it at 1 evening room temperature, it was immersed in ethyl acetate for 30 minutes, and the amount of remaining extraction was shown in a table 4. Moreover, the condition of this mixed resin solution was shown in a table 4.

(Examples 2-9) The rest performed the same actuation as an example 1 using the resin solution which showed the resin solution shown in a table 5 in a table 5 instead of the resin (B1-1) solution of an example 1 instead of the resin (A-1) solution of an example 1. The result was shown in a table 6.

(Examples 10 and 11) Instead of PGE of an example 1, the rest performed the same actuation as an example 1 using the compound (C) shown in a table 5. The result was shown in a table 6.

(Examples 12 and 13) The rest performed the same actuation as an example 1 by the daily dose which showed the amount of a resin (A-1) solution and the resin of resin (B1-1) in a table 5 among examples 1. The result was shown in a table 6.

(Example 14) Further, 20g (TMP) of trimethylolpropane triacrylate was added, and the rest showed the result of having performed the same actuation as an example 1 to the presentation of an example 1, according to a table 6.

[0034] (Examples 1-3 of a comparison) By the presentation shown in a table 5, the result of having operated it was shown by the same assessment approach as an example 1 according to a table 6.

[0035]

Table 5----- Example Resin (A) solution Resin (B) solution Compound (C) ----- 1 (A-1) (B1-1) PGE 2 (A-1) (B1-2) PGE 3 (A-1) (B1-3) PGE 4 (A-1) (B-2 -1) PGE 5 (A-1) (B-2 -2) Nothing 6 (A-2) (B1-1) PGE 7 (A-3) (B1-1) PGE8 (A-4) PGE (B1-1) 9 (A-5) (B1-1) PGE10 (A-1) GMA (B1-1)11 (A-1) (B1-2) GMA12 (A-1) PGE (B1-1)13 (A-1) (B1-1) Example of PGE14 (A-1) PGE (B1-1) comparison 1 Nothing (A-1) Example 2 of a PGE comparison Nothing (B1-1) Example 3 of a PGE comparison (A-1) (B1-1) Nothing ----- [0036]

A table 6 ----- Example The amount of ethyl-acetate remaining extraction (%) The condition of the coating liquid of one week after ----- 1 90 Good 2 88 Good 3 90 Good 4 85 Fitness 5 75 Good 6 85 Good 7 80 Good 8 80 is good. 9 80 Fitness 10 85 Fitness 11 80 Fitness 12 80 Fitness 13 80 Fitness 14 95 Example 1 of a good comparison 0 Example 2 of a good comparison 0 Example 3 of a good comparison 0 Fitness ----- [Effect of the Invention] By this invention, it excels in preservation stability and the resin constituent which can be hardened at a room temperature is offered.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The hardenability resin constituent with which the weight average molecular weight to which it comes to carry out the Michael addition reaction of the (Compound b) 5-80 % of the weight to which it has an acrylic radical or two or more methacrylic radicals in 1 molecule, and weight average molecular weight has two or more active hydrogen of amino nature in less than 1000 (Compound a) 20-95 % of the weight and 1 molecule consists of the resin (A) of 1,000-1,000,000, resin (B1) which has active hydrogen other than the amino group, and a compound (C) which has an epoxy group.

[Claim 2] The hardenability resin constituent with which the weight average molecular weight to which it comes to carry out the Michael addition reaction of the (Compound b) 5-80 % of the weight to which it has an acrylic radical or two or more methacrylic radicals in 1 molecule, and weight average molecular weight has two or more active hydrogen of amino nature in less than 1000 (Compound a) 20-95 % of the weight and 1 molecule consists of resin (B-2) which has the active hydrogen and the epoxy groups other than the resin (A) of 1,000-1,000,000, and the amino group.

[Claim 3] The hardenability resin constituent according to claim 1 or 2 characterized by active hydrogen other than the amino group being the methine hydrogen or methylene hydrogen permuted by two pieces or three functional groups which are independently chosen from a carbonyl group, a carboxyl group, a carbamoyl group, a cyano group, or a nitro group.

[Claim 4] Furthermore, the hardenability resin constituent according to claim 1 to 3 characterized by including a compound (a) one to 80% of the weight to the whole resin constituent.

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(54)【発明の名称】 硬化性樹脂組成物

(57)【要約】

【課題】保存安定性にすぐれ、室温で硬化可能な樹脂組成物を提供する。

【解決手段】1分子中にアクリル基またはメタクリル基を2個以上有し、重量平均分子量が1000未満の化合物(a)20~95重量%、および、1分子中にアミノ性の活性水素を2個以上有する化合物(b)5~80重量%をマイケル付加反応させてなる樹脂(A)、アミノ基以外の活性水素を有する樹脂(B1)、および、エポキシ基を有する化合物(C)からなる硬化性樹脂組成物。

【特許請求の範囲】

【請求項1】 1分子中にアクリル基またはメタクリル基を2個以上有し、重量平均分子量が1000未満の化合物(a) 20~95重量%、および、1分子中にアミノ性の活性水素を2個以上有する化合物(b) 5~80重量%をマイケル付加反応させてなる重量平均分子量が1,000~1,000,000の樹脂(A)、アミノ基以外の活性水素を有する樹脂(B1)、および、エポキシ基を有する化合物(C) からなる硬化性樹脂組成物。

【請求項2】 1分子中にアクリル基またはメタクリル基を2個以上有し、重量平均分子量が1000未満の化合物(a) 20~95重量%、および、1分子中にアミノ性の活性水素を2個以上有する化合物(b) 5~80重量%をマイケル付加反応させてなる重量平均分子量が1,000~1,000,000の樹脂(A)、および、アミノ基以外の活性水素およびエポキシ基を有する樹脂(B2) からなる硬化性樹脂組成物。

【請求項3】 アミノ基以外の活性水素が、カルボニル基、カルボキシル基、カルバモイル基、シアノ基、またはニトロ基から独立して選ばれる2個または3個の官能基で置換されたメチン水素またはメチレン水素であることを特徴とする請求項1または2記載の硬化性樹脂組成物。

【請求項4】 さらに、化合物(a) を樹脂組成物全体に対して、1~80重量%含むことを特徴とする請求項1~3のいずれかに記載の硬化性樹脂組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、塗料、接着剤、粘着剤、インキ、充填剤、成形材料用の利用される、塗布または型中に注入後、室温で硬化する樹脂組成物に関する。

【0002】

【従来の技術】 アセトアセトキシ基に代表される、カルボニル基などの活性水素を利用した硬化性樹脂組成物は、USP4,408,018号公報、特開平1-121341号公報、特開平1-204919号公報、USP5,017,649号公報、特開平6-167355号公報、特開平7-173262号公報などに例示されている。これらは、それぞれ、硬化触媒に特徴をもっているが、いずれも、硬化触媒が樹脂と相互に混ざらない、室温では十分な硬化を示さない、あるいは、塗布前の塗工液の状態で1週間以上の保存ができないという問題点があった。

【0003】

【発明が解決しようとする課題】 発明者らは、エポキシ化合物およびアミン性活性水素と(メタ)アクリル基との反応によって得た樹脂の混合物が、活性水素と(メタ)アクリル基との反応を著しく促進することを見出し

た。そして、これを使用して、室温で放置するだけで、硬化可能であり、保存安定性に優れた樹脂組成物を提供するものである。

【0004】

【課題を解決するための手段】 本発明は、1分子中にアクリル基またはメタクリル基を2個以上有し、重量平均分子量が1000未満の化合物(a) 20~95重量%、および、1分子中にアミノ性の活性水素を2個以上有する化合物(b) 5~80重量%をマイケル付加反応させてなる重量平均分子量が1,000~1,000,000の樹脂(A)、アミノ基以外の活性水素を有する樹脂(B1)、および、エポキシ基を有する化合物(C) からなる硬化性樹脂組成物に関する。また、1分子中にアクリル基またはメタクリル基を2個以上有し、重量平均分子量が1000未満の化合物(a) 20~95重量%、および、1分子中にアミノ性の活性水素を2個以上有する化合物(b) 5~80重量%をマイケル付加反応させてなる重量平均分子量が1,000~1,000,000の樹脂(A)、および、アミノ基以外の活性水素およびエポキシ基を有する樹脂(B2) からなる硬化性樹脂組成物に関する。また、アミノ基以外の活性水素が、カルボニル基、カルボキシル基、カルバモイル基、シアノ基、またはニトロ基から独立して選ばれる2個または3個の官能基で置換されたメチン水素またはメチレン水素であることを特徴とする上記硬化性樹脂組成物に関する。さらに、化合物(a) を樹脂組成物全体に対して、1~80重量%含むことを特徴とする上記硬化性樹脂組成物に関する。

【0005】

【発明の実施の形態】 本発明で使用される、1分子中にアクリル基またはメタクリル基を2個以上有し、重量平均分子量が1000未満の化合物(a) としては、例えば、多官能アルコールまたは多官能フェノールのポリ(メタ)アクリル酸エステルが挙げられる。

【0006】 具体的には、エチレングリコール、プロピレングリコール、ジエチレングリコール、ジプロピレングリコール、トリエチレングリコール、トリプロピレングリコール、テトラエチレングリコール、テトラプロピレングリコール、ポリエチレングリコール、ポリプロピレングリコール、ブタンジオール、2,2-ジメチルプロパンジオール、ペンタンジオール、ヘキサンジオールなどの二官能アルコールのジ(メタ)アクリレート、

【0007】 フタル酸、ヘキサヒドロフタル酸、マレイン酸、コハク酸、マロン酸、ヘキサン二酸などの二官能カルボン酸のポリアルキレングリコール変性物またはエビクロヒドリン変性物のジ(メタ)アクリレート、トリメリット酸、ピロメリット酸、ヘキサヒドロピロメリット酸などの3価以上のカルボン酸のポリアルキレングリコール変性物またはエビクロヒドリン変性物のポリ(メタ)アクリレート、ビスフェノールA誘導体のエビクロ

ルヒドリン変性物のジ(メタ)アクリレート、イソシマル酸誘導体のポリアルキレングリコール変性物のポリ(メタ)アクリレート、

【0008】グリセリン、トリメチロールアロパン、ペンタエリスリトール、ジペンタエリスリトール、マンニトール、ソルビトールなどの多官能アルコール、またはそのポリアルキレングリコール変性物、または、エピクロヒドリン変性物のポリ(メタ)アクリート、カテコール、レブリン、ヒドロキノ、フロログリシン、ピロガロールなどの多官能フェノールのポリ(メタ)アクリレートなどが挙げられる。これらは、2種以上用いてもよい。

【0009】また、本発明で使用する、1分子中にアミノ性の活性水素を2個以上有する化合物(b)としては、アンモニアのほか、メチルアミン、エチルアミン、プロピルアミン、ブチルアミン、ペンチルアミン、ヘキシルアミン、シクロヘキシルアミン、ヘプチルアミン、オクチルアミン、メチルヒドラジン、エチルヒドラジン、ベンジルアミン、フェネチルアミン、N、N-ジメチルプロピルアミンなどのアルキレン鎖、および1級アミノ基を1個有するアミン、メトキシエトキシエチルアミン、メトキシプロピルプロピルアミン、メトキシポリエチレンオキシエチルアミンなどのポリアルキレン鎖、および1級アミノ基を1個有するアミン、エチレンジアミン、プロピレンジアミン、1,6-ヘキサジアミン、ジエチレントリアミン、トリエチレントトラミン、メラミンなど、1級アミノ基を2個以上有するアミン、N、N'-ジメチルエチレンジアミンなど2級アミノ基を2個以上有するアミン、また、ピペラジンなどの環状アミン、アリルアミンなどの不飽和二重結合を有するアミン、エタノールアミンなどの官能基を有するアミンなどが挙げられる。また、上記1級アミノ基を2個以上有するアミンを、例えば、エチルアクリレートまたは塩化メチルなどで、一部の活性水素を置換して得られる、2個以上の2級アミノ基を有する化合物を用いてもよい。これらのアミンは、2種以上用いてもよい。

【0010】本発明で使用する樹脂(A)は、1分子中にアクリル基またはメタクリル基を2個以上有し、重量平均分子量が1000未満の化合物(a)20~95重量%、および、1分子中に1個以上の1級アミノ基、または2個以上の2級アミノ基を有する化合物(b)5~80重量%を反応させて得られる。この反応は、化合物(a)の(メタ)アクリル基と、化合物(b)のアミノ基の間で、マイケル付加させることによる重合反応である。マイケル付加反応は、一般に知られているように、化合物(a)および化合物(b)を、常圧で、容器内で攪拌または振動させて反応させる。樹脂(A)は、無溶媒中でも合成可能であるが、N、N-ジメチルホルムアミド、N、N-ジメチルアセトアミド、ヘキサメチルホスホラストリアミドなどのアミド系溶媒、メタノー

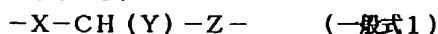
ル、エタノール、アロパノール、ブタノールなどのアルコール系溶媒、ジエチルエーテル、ジオキサン、テトラヒドロフランなどのエーテル系溶媒、あるいは水などの溶媒中を用いると、反応速度が向上する。

【0011】反応時の温度は化合物(a)がアクリル基を含む時は、室温で反応して樹脂(A)となるが、分子量向上のために、室温で放置後、溶媒環流温度まで、加熱してもよい。反応時間は、5分から3日程度の条件で反応させる。得られた樹脂(A)は、石油エーテル、ヘキサンなどで沈降精製を行い、低分子量成分を除去すると、硬化後の物性が向上し、好ましい。

【0012】樹脂(A)の重量平均分子量は、例えば、GPC(ゲル浸透クロマトグラフィ)でスチレン換算で、1,000~1,000,000であることが好ましい。より好ましくは、3,000~500,000である。これより小さい場合には、低分子量成分により硬化が不良となることがある。また、これより大きい場合は、樹脂(B)との相溶性が悪くなる。樹脂(A)の重量平均分子量を、1000以上にするためには、化合物(a)として1分子中に(メタ)アクリル基を3個以上有する化合物、または、化合物(b)として1分子中にアミノ性の活性水素を3個以上有する化合物を、併用することが推奨される。

【0013】樹脂(A)を合成する際には、化合物(a)と、化合物(b)の配合量比は、理論的には、化合物(a)の(メタ)アクリル基の化学当量と、化合物(b)のアミノ性の活性水素の化学当量が等しいのが好ましいはずである。しかし、実際には、反応液の粘度などの影響があり、必ずしも、硬化性に化学当量の比率は関係していない。そのため、樹脂(A)の重量平均分子量を1000以上にするためには、化合物(a)20~95重量%、および、化合物(b)5~80重量%の間で、その組み合わせの最適値を選択することになる。

【0014】次に、本発明で使用するアミノ基以外の活性水素を有する樹脂(B1)、および、アミノ基以外の活性水素およびエポキシ基を有する樹脂(B2)のアミノ基以外の活性水素とは、水酸基、メルカプト基、カルボキシル基のほか、一般式1で示すような活性水素が挙げられる。



(ここで、X、Y、Zは、特に限定はないが、少なくとも1つは、カルボニル基、カルボキシル基、カルバモイル基、シアノ基、またはニトロ基から選ばれる官能基を示す。)

【0015】活性水素が、カルボニル基、カルボキシル基、カルバモイル基、シアノ基、またはニトロ基から、独立して選ばれる2個以上の官能基で置換されたメチン水素、またはメチレン水素であることが、特に、好ましい。これは、上記一般式1では、X、Y、Zのうち、少なくとも2つが上記官能基を有する場合である。このよ

うな活性水素として、マロン酸残基(X、Z=カルボキシル基、Y=H)、アセトアセチル基(X=カルボニル基、Y=H、Z=カルボキシル基)、アセトカルバモイル基(X=カルボニル基、Y=H、Z=カルバモイル基)、シアノ酢酸残基(X=シアノ基、Y=H、Z=カルボキシル)、ニトロ酢酸残基(X=ニトロ基、Y=H、Z=カルボキシル基)などが挙げられる。

【0016】樹脂(B1)または樹脂(B2)が、これらの活性水素を有するためには、これらの活性水素を有するモノマを重合させて得る方法がある。例えば、2-ヒドロキシエチル(メタ)アクリレート、2-メルカプトエチル(メタ)アクリレート、(メタ)アクリル酸、アセトアセトキシエチル(メタ)アクリレートなどの活性水素を有する(メタ)アクリル酸エステルをビニル重合させる方法がある。

【0017】また、上記、活性水素を有する(メタ)アクリル酸エステルに、さらに、スチレン、ビニルピリジン、ビニルピロリドン、酢酸ビニルなどのビニルモノマ、(メタ)アクリル酸アルキルエステル、(メタ)アクリル酸ポリ(アルキルオキシ)エステルなどの(メタ)アクリルモノマとの共重合体も好適に用いられる。

【0018】樹脂(B2)の場合は、さらに、グリシジル(メタ)アクリレートなどのエポキシ基を有するモノマを共重合させる必要がある。

【0019】このほか、末端に、水酸基を有するエポキシ樹脂、フェノキシ樹脂、繰返し単位に水酸基を有する、ビスフェノール誘導体とエピクロロヒドリン誘導体の重合体などが樹脂(B1)の例として挙げられる。また、樹脂(B1)と樹脂(B2)を、混合して用いてもよい。

【0020】樹脂(B)の重量平均分子量は、例えば、GPC(ゲル浸透クロマトグラフィ)でスチレン換算で、1,000~2,000,000であることが好ましい。より好ましくは、10,000~1,000,000である。これより小さい場合には、低分子量成分により硬化が不良となることがある。また、これより大きい場合は、樹脂(A)との相溶性が悪くなる。

【0021】本発明で使用されるエポキシ基を有する化合物(C)は、エピクロロヒドリン、フェニルグリシジルエーテル、スチレンオキサイド、シクロヘキセンオキサイド、ブテンオキサイド、グリシジル(メタ)アクリレート、グリシジルシナメート、アリルフェニルエーテル、ビニルシクロヘキセンモノエポキシサイド、1,3-ブタジエンモノエポキシサイドなどが挙げられる。これらは、2種以上用いてもよい。

【0022】化合物(C)は、樹脂(A)、樹脂(B1)または樹脂(B2)の樹脂全体に対して、1~10重量%の比率で加えて用いるのが好ましい。樹脂(B2)を用いた場合は、化合物(C)は必須ではないが、*

*好適に用いられる。この場合、樹脂(B2)のエポキシモノマと、化合物(C)の合計が樹脂全体に対して1~100重量%の比率で加えて用いるのが好ましい。

【0023】本発明の樹脂組成物の硬化性を向上するために、前記化合物(a)を、樹脂全体に対して1~80重量%の比率で加えて用いることが好ましい。

【0024】樹脂(A)、樹脂(B1)または樹脂(B2)、および必要に応じて、化合物(C)または化合物(a)は、容器内で攪拌、回転、または振動させて混合して樹脂組成物とさせる。このとき、150℃以下の熱を加えて、均一な混合を促進してもよい。また、チタン白、各種顔料などの着色剤、滑剤などを添加してもよい。光処理する場合は、さらに、各種増感色素を添加してもよい。

【0025】本発明の樹脂組成物は、室温で硬化するが、熱、光または電子線の処理により、硬化を促進させてもよい。熱処理する場合は、250℃以下で加熱する。熱源に特に限定はないが、一般的には、熱循環式オーブン、あるいは、加熱ロールが用いられる。光処理する場合、光源に特に限定はなく、水銀ランプ、キセノンランプ、メタルハライドランプ、蛍光灯、白熱灯、各種レーザなどが挙げられる。また、電子線で処理する場合は、各種の中低圧電子加速器が用いられる。

【0026】

【実施例】次に本発明を実施例により、更に詳細に説明するが、本発明はこれに限定されるものではない。

【0027】(合成例1)ブチルアミン(BA)3.65g、2,2-ジメチルプロパン1,3-ジオールジアクリレート(NP)5.31g、および、トリメチロールプロパントリアクリレート(TMP)7.41gをメタノール15.0g中で、室温で、1晩攪拌して、樹脂(A-1)溶液を得た。その重量平均分子量を表2に示した。

(合成例2~5)合成例1のブチルアミンの代わりに、表1に示した化合物(b)を、合成例1の2,2-ジメチルプロパン1,3-ジオールジアクリレートの代わりに表1に示した化合物(a)を用いて、樹脂溶液(A-1)~(A-10)を得た。その重量平均分子量を表2に示した。なお表中、HAはヘキシルアミン、OAオクチルアミン、9EGは、ポリエチレングリコールジアクリレート(共栄社化学製)、BPはアロピレンオキサイド変性ビスフェノールAジアクリレート(共栄社化学製)、DCPは水添ジシクロペンタジエニルジアクリレート(共栄社化学製)、PE3は、ペンタエリスリトールトリアクリレート、PE4は、ペンタエリスリトールテトラアクリレート、DPEはジベンタエリスリトールヘキサアクリレートを示す。

【0028】

合成例 (樹脂溶液)	化合物 (a) () 内は、g数	化合物 (b) () 内は、g数
1 (A-1)	BA(3.65)	NP(5.31) TMP(7.41)
2 (A-2)	BA(3.65)	NP(6.37) TMP(5.93)
3 (A-3)	BA(3.65)	9EG(13.06) PE3(7.45)
4 (A-4)	HA(5.06)	BP(14.22) PE4(8.81)
5 (A-5)	OA(6.46)	DCP(7.55) DPE(14.46)

【0029】

表2

合成例 (樹脂溶液)	スチレン換算重量平均分子量
1 (A-1)	3.0×10 ³
2 (A-2)	2.5×10 ³
3 (A-3)	2.0×10 ³
4 (A-4)	3.5×10 ³
5 (A-5)	4.0×10 ³

【0030】(合成例6) 2-アセトアセトキシエチルメタクリレート (AAEM) 50gと、メチルメタクリレート (MMA) 50g、アゾビスイソブチロニトリル 3gを酢酸エチル100gに溶解し、窒素雰囲気下、環流温度で8時間反応させて、樹脂溶液 (B1-1) を得た。

(合成例7~10) 合成例6の2-アセトアセトキシエチルメタクリレートと、メチルメタクリレートの代わりに、*

*表3に示したモノマを用いて、樹脂溶液 (B1-2) ~ (B2-2) を得た。その重量平均分子量を表4に合わせて示した。表中、STはスチレン、CAEMは2-シアノアセトキシエチルメタクリレート、BMAはブチルメタクリレート、GMAはグリシジルメタクリレート、HEMAは2-ヒドロキシエチルメタクリレートを表す。

【0031】

表3

合成例 (樹脂溶液)	モノマ () 内はg数
6 (B1-1)	AAEM(50) MMA(50)
7 (B1-2)	AAEM(50) ST(50)
8 (B1-3)	CAEM(50) BMA(50)
9 (B2-1)	AAEM(50) MMA(45) GMA(5)
10 (B2-2)	HEMA(5) MMA(90) GMA(5)

【0032】

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表4

合成例 (樹脂溶液)	スチレン換算重量平均分子量
6 (B1-1)	4.7×10 ⁴
7 (B1-2)	5.4×10 ⁴
8 (B1-3)	4.6×10 ⁴
9 (B2-1)	6.0×10 ⁴
10 (B2-2)	6.5×10 ⁴

【0033】(実施例1) 樹脂(A-1) 溶液100g、樹脂(B1-1) 溶液100g、およびフェニルグリシジルエーテル(PGE) 20gを、室温で3時間攪拌混合後、ガラス板に厚さ50 μ mでキャスト塗工し、1晩室温で、乾燥させたのち、酢酸エチルに、30分浸漬し、抽出残量を表4に示した。また、この混合樹脂溶液の状態を表4に示した。

(実施例2~9) 実施例1の樹脂(A-1) 溶液の代わりに、表5に示した樹脂溶液を、実施例1の樹脂(B1-1) 溶液の代わりに表5に示した樹脂溶液を用いて、

あとは、実施例1と同様の操作を行った。その結果を表6に示した。

(実施例10, 11) 実施例1のPGEの代わりに、表5に示した化合物(C)を用いて、あとは、実施例1と*

*同様の操作を行った。その結果を表6に示した。

(実施例12, 13) 実施例1のうち、樹脂(A-1) 溶液と、樹脂(B1-1) の樹脂の量を、表5に示した分量で、あとは、実施例1と同様の操作を行った。その結果を表6に示した。

(実施例14) 実施例1の組成に、さらに、トリメチロールプロパントリアクリレート(TMP)を20g加え、あとは実施例1と同様の操作を行った結果を表6に合せて示した。

【0034】(比較例1~3) 表5に示した組成で、実施例1と同様の評価方法で、操作を行った結果を、表6に合せて示した。

【0035】

表5

実施例	樹脂(A) 溶液	樹脂(B) 溶液	化合物(C)
1	(A-1)	(B1-1)	PGE
2	(A-1)	(B1-2)	PGE
3	(A-1)	(B1-3)	PGE
4	(A-1)	(B2-1)	PGE
5	(A-1)	(B2-2)	なし
6	(A-2)	(B1-1)	PGE
7	(A-3)	(B1-1)	PGE
8	(A-4)	(B1-1)	PGE
9	(A-5)	(B1-1)	PGE
10	(A-1)	(B1-1)	GMA
11	(A-1)	(B1-2)	GMA
12	(A-1)	(B1-1)	PGE
13	(A-1)	(B1-1)	PGE
14	(A-1)	(B1-1)	PGE
比較例1	(A-1)	なし	PGE
比較例2	なし	(B1-1)	PGE
比較例3	(A-1)	(B1-1)	なし

【0036】

表6

実施例	酢酸エチル抽出残量(%)	1週間後の塗工液の状態
1	90	良好
2	88	良好
3	90	良好
4	85	良好
5	75	良好
6	85	良好
7	80	良好
8	80	良好
9	80	良好

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10	85	良好
11	80	良好
12	80	良好
13	80	良好
14	95	良好
比較例1	0	良好
比較例2	0	良好
比較例3	0	良好

【発明の効果】本発明により、保存安定性にすぐれ、室*10*温で硬化可能な樹脂組成物が提供される。

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